SYNTHESIS AND CHARACTERIZATION OF POLYMER GEL ELECTROLYTE

A Thesis

Submitted by

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Under the guidance of

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Declaration

I hereby declare that the work carried out in this thesis is entirely original. It was carried out by me along with Miss Swagatika Bhoi, and Mr Manoranjan Samal at the Department of Physics, National Institute of Technology, Rourkela. I further declare that it has not formed the basis for the award of any degree, diploma or similar title of any university or institution.

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Certificate

This is to certify that the thesis entitled **"SYNTHESIS AND CHARACTERIZATION OF POLYMER GEL ELECTROLYTE"** is a bonafide work of **Miss Paradarsini Parida**, in partial fulfillment of the requirements for the award of the degree of Master of Science in Physics at National Institute of Technology, Rourkela carried out by her under our supervision. To the best of our knowledge, the experimental matter embodied in the thesis has not been submitted to any other University/Institute for the award of any degree or diploma.

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My hearty thanks to my parents for their blessings, inspiration and moral support.

Date: Paradarsini Parida

Dedicated to my

Alma Mater

Contents

Abstract

A series of polymer gel electrolyte with a wide range of concentrations of solvent to salt ratio have been prepared by the gelation method with suitable choice of polymer (PVdF), solvent (DMF) and salt (NaI). The presence of both crystalline and amorphous phases (i.e. semi-crystalline nature) was observed from XRD graph. Further this observation was confirmed by SEM micrographs. The dielectric and electrical properties of the material were studied by the dielectric spectroscopic technique in a wide frequency range at room temperature. The relative dielectric constant decreases with increase in frequency. The graph of a.c. conductivity versus frequency for different concentrations showed a frequency independent plateau in the higher frequency region and dispersion in the lower frequency region. The complex impedance plot explained the bulk properties of the material in the high frequency region which further helped in calculating the d.c. conductivity.

Chapter 1

Introduction

1.1 ELECTROLYTE

All the electrochemical storage and conversion devices such as batteries, fuel cells, super-capacitors etc. have mainly three components i.e. (i) cathode, (ii) anode and (iii) electrolyte. Now-a-days, liquid electrolyte is mainly used in most of the electrochemical devices. Electrolyte is any substance containing free ions that makes it conductive. Electrolytic solutions are normally formed when a salt is placed in a polar solvent such as water and the individual components dissociate due to the thermodynamic interactions between solvent and solute molecules. For example, when NaCl is added to water, the salt dissociates into its component ions as in the chemical reaction: $NaCl_{(s)} \rightarrow Na^{+}_{(aq)} + Cl^{-}_{(aq)}$ where 's' stands for solid and 'aq' stands for aqueous. Thus, the substance becomes ions in solution and acquires the capacity to conduct electricity.

1.2 WHY DO WE NEED SOLID ELECTROLYTE?

Liquid electrolytes have a number of shortcomings such as (i) they cannot be operated in a wide range of temperature, (ii) failure of the device due to corrosion of the electrolyte by electrolytic solution, (iii) low energy and power density and (iv) also its bulky size. Also liquid electrolytes tend to leak out of the cells into which they are sealed for which solid electrolyte is required so as to eliminate these discrepancies. Solid electrolytes are free from the problem of leakage and are intended to replace the liquid electrolyte.

1.3 SOLID ELECTROLYTE

The solids exhibiting high ionic conductivity are called solid electrolytes. The conductivity of typical solid electrolytes lies in the range of $10^{-6} \leq \sigma \leq 10^{-1}$ S cm^{-1} which is same as that of dilute aqueous ionic solutions. The conductivity values of many solid electrolytes are close to those of liquid electrolytes and also remain stable for a wide range of temperature. For electrochemical device applications, it should possess the following ideal properties [1] such as (i) ionic conductivity should be very high (approximately 10^{-1} to 10^{-4} S cm^{-1}) and electronic conductivity should be negligibly small ($<10^{-6}$ S cm^{-1}), (ii) the activation energy should be

very low (<0.3 eV), and (iii) the only charge carriers should be ions i.e. ionic transference number, $t_{ion} \approx 1$. Various structural and non-structural factors are responsible for the above characteristic properties of solid electrolytes [2]. Some important factors include the crystal structure, high degree of lattice disorder, structure-free volume, high mobile ion concentration, size of mobile ions, ionic polarization, ionic interactions, bonding characteristics, vibrational amplitudes or rotational motion of neighboring ions, number and accessibility of occupancy sites, etc.

1.4 CLASSIFICATION OF SOLID ELECTROLYTE

On the basis of different microstructure and physical properties solid electrolytes are categorized into four types:

1. Framework crystalline materials
2. Amorphous-glassy electrolytes
3. Polymer electrolytes
4. Composite electrolytes

Framework crystalline materials are ordered while the rest three are disordered. Amorphous-glassy and polymer electrolytes are microscopically disordered whereas composite electrolytes are macroscopically disordered materials.

1.4.1 Framework crystalline materials: They consist of a crystalline skeleton of more or less rigid mobile ions. They are categorized into two types [3, 4].

Soft-framework crystals: The bonding is mostly ionic. The mobile ions are highly polarizable and heavy. They have low Debye temperatures and melting points in which the conduction is due to ion hopping or liquid-like diffusion. A sharp ionic order-disorder phase transition appears between the low and high conducting phases. Some examples of soft-framework crystals are AgI, CuI, etc.

Hard-framework crystals: The bonding is covalent, has low polarizability of mobile ions and has high Debye temperatures and melting points. There is less sharp or absence of the order-disorder phase transition. In these materials conductivity is due to mobile ions hopping through the favourable sites of the framework. They are usually oxides.

It is most extensively studied both in single and polycrystalline form as evident from different sources. Polycrystalline materials are mostly used in technological applications simply because they are easy to prepare and cost of preparation is less [5].

1.4.2 Amorphous-glassy electrolytes: They are ion-conducting glasses and have several advantages over the crystalline electrolytes. They have variable compositions and high ionic conductivity. The grain boundaries are absent and there is possibility of fabrication in the form of thin-film. Melt quench technique or sol-gel methods are used for the preparation of these electrolytes [6, 7].

1.4.3 Polymer electrolytes: Solid polymer electrolytes are formed by complexation of polar polymers like PEO (polyethylene oxide), PPO (polypropylene oxide), PEG (polyethylene glycol) etc. with ionic salts having low lattice energy and bulky anions [8]. They are mostly prepared by solution-cast method, electro-deposition method or sol-gel method. These electrolytes showed fast-ion conduction behaviour only above glass transition temperature. Below the glass transition, the ionic conductivity drops as the chain motion in the polymer segments do not occur. It has several advantages such as thin film forming property, better processability, good flexibility, light weight, elasticity and transparency. They have less mechanical strength, workability, time stability, ionic conductivity, etc [9]. Both anions and cations can be mobile in polymer electrolytes [10]. To improve the electrical conductivity and mechanical stability of polymer electrolytes several methods such as (i) copolymerization in which a polymer having low T_g is added to the host polymer, (ii) plasticization in which a low molecular weight polymer like PEG, PEO, PC, EC, etc are added to the host polymer, (iii) dispersion of organic or inorganic fillers into the host polymer, and (iv) radiation of gamma rays are adopted.

1.4.4. Composite electrolytes: They are multi-phase (mostly two-phase) solid system in which two or more materials are mixed together to achieve some desirable material with better conductivity. They are prepared by dispersing sub-micrometer size particles of insulating and chemically inert materials i.e. the second phase dispersoids into a moderate-ionic conducting solid called first phase host matrix.

1.5 POLYMER ELECTROLYTE

The famous work on solid polymer electrolytes was started by Fenton *et. al*. The potential applications of these materials were realized towards the late '70s. It involves a variety of transporting ions such as H^+, Li^+, Na^+, K^+, Ag^+ etc. The advantages of these electrolytes are that there is no internal shorting, no leakage of electrolytes, casing economy and no non-combustible reaction products are formed at the electrode surface. They possess transport properties alike liquid ionic solutions at the microscopic level, but they are solid at macroscopic level. They find applications in lithium ion rechargeable batteries and other electrochemical devices.

1.6 TYPES OF POLYMER ELECTROLYTE

Polymer electrolytes are categorized as [11, 12]:

1. Dry solid polymer electrolyte (dry SPE)
2. Plasticized polymer electrolyte
3. Polymer gel electrolyte
4. Composite polymer electrolyte

Dry solid polymer electrolyte is prepared by dissolving ionic salt into coordinating polar polymer hosts such as PEO, PPO [13, 14]. Casting of the film is done either by usual cast method or by hot-press technique.

Plasticized polymer electrolyte is prepared by adding liquid (low molecular weight) plasticizer with dry SPE. The magnitude of ambient temperature conductivity gets enhanced as compared to solid polymer electrolytes, but the mechanical stability is deteriorated. There is an increased corrosive reactivity of polymer electrolyte towards the electrode-electrolyte interface.

Polymer gel electrolyte is formed by dissolving a salt in polar liquid and adding a polymer network to give the material mechanical stability. It is neither liquid nor solid or conversely we can say it is both liquid and solid. It possesses both cohesive properties of solids and the

diffusive property of liquids on the virtue of which it has various important applications. It offers high ambient temperature ionic conductivity. Mechanical stability is deteriorated in gel electrolyte.

Composite polymer electrolyte is prepared by dispersing small fraction of micro/nano-size inorganic/organic filler particles with conventional SPE host [15, 16]. As a consequence of dispersion, the ionic conductivity and the mechanical stability gets enhanced.

1.7 DIFFERENT TYPES OF POLYMER HOSTS

1.7.1 Poly-ethylene oxide (PEO): PEO-based electrolytes have very low ionic conductivity that ranges from 10^{-8} to 10^{-4} S cm^{-1} at temperatures between 40 and 100^{0} C [17, 18]. In order to improve the room temperature ionic conductivity, the role of various additives such as filler, plasticizer were examined [19]. It was found that partial substitution of high polymer by a PEO of low molecular weight had the effect of increasing the solubility of the crystalline polymer in the liquid polymer as well as lowering the effective melting and glass transition temperature of the polymer [20].

1.7.2. Poly methyl meth-acrylate (PMMA): It was found that PMMA could be used as a gelating agent. Later the researchers focused on gel PMMA electrolytes with different plasticizers [21]. The addition of PMMA in various proportions increased the viscosity of the macromolecule solution. On contrary, upon the addition of PMMA the conductivity reduced considerably but the room temperature conductivity remained unvaried and it was close to the conductivity of liquid electrolyte. At ambient temperature, it was observed that the ionic conductivity decreased with increasing amount of polymer. The decrease in ionic conductivity and an increase in activation energy at high concentration were due to some interactions between the polymer chain and the conducting electrolytes.

1.7.3. Poly vinylidene-fluoride (PVdF): Due to its attractive properties it has been chosen as a polymer host for lithium battery applications. Polymer electrolytes hosted by PVdF are highly stable due to the presence of strong electron-withdrawing functional group (-C-F) and it has a dielectric constant which helps for greater dissolution of lithium salts and supports high concentration of charge carriers [22]. These electrolytes exhibit low ionic conductivity

of the order of 10^{-5} S cm^{-1} at elevated temperatures and are attributed to inhomogenity of the membrane at or below ambient temperature [23, 24]. The PVdF-based electrolytes offer excellent electrochemical properties and these are not stable towards lithium which leads to poor interfacial properties between lithium and fluorine.

1.8 ELECTRICAL CONDUCTIVITY

From the knowledge of temperature dependent conductivity studies, it has been observed that polymer electrolytes exhibit two dominant conduction mechanisms [25] which divide these materials into two separate groups.

One group of polymer electrolytes obeys Vogal-Tamman-Fulcher (VTF) relationship governed by the relation:

$$\sigma = AT^{-1/2}\exp[-E_a/(T-T_0)]$$

where, A is pre-exponential factor, E_a is the pseudo activation energy, T_0 is the equivalent glass transition temperature i.e. it is nearly 50^0C less than the glass transition temperature.

The other group follows the Arrhenius type equation governed by the relation:

$$\sigma=\sigma_0 \exp(-E_a/kT)$$

E_a can be computed from log σ versus 1/T plot which indicates ion transport via a simple hopping mechanism.

1.9. POLYMER GEL ELECTROLYTE

Generally, gel electrolyte is formed by dissolving a salt in a polar liquid and adding an inactive polymeric material to give the material mechanical stability. The Polymer gel electrolytes are flexible solid electrolytes with potential use in applications such as rechargeable lithium batteries, sensors and display devices. The polymer gel electrolytes consists of three components; polymer, solvent, and ionic salt. The salt provides ions for conducting and also it has low lattice energy, the solvent helps in dissolution of the salt as it has a higher dielectric constant, Ɛ and hence provides the medium for ion conduction. It generally has the active oxygen which helps in the formation of the coordinate bond. The polymer works as a container that can hold a large amount of solvent and processes the characteristics of both liquids and solids. It has high molecular weight and also provides

mechanical strength and flexibility. Gel polymer electrolyte systems are an attempt to strike a balance between the high conductivity of organic liquid electrolytes and the dimensional stability of solid polymer electrolytes. The design of such gel systems depends on an understanding of the mechanism of ionic conduction in gels and on the ability to tune the structure of the polymer component in the gel to optimize the overall physical properties. Polymer gel electrolytes are frequently used as electrolyte films for flexible and dry ionic devices like in lithium batteries, super-capacitors and electrochemical devices. It is widely used because of its high conductivity. It can replace liquid electrolyte as they have high chemical and electrical stability as compared to liquid electrolyte and it prevents the devices from drying out or leaking electrolyte. Advantage of gel electrolyte is its high ionic conductivity required for device application while the disadvantage is the poor mechanical stability and compatibility between electrolyte-electrode interface.

1.10 LITERATURE SURVEY

In 1973, Wright *et. al* first reported the complexation formed between PEO and few sodium and potassium salts. Thin films of the complexes were prepared and were maintained at 150^0C for 24 hours under vacuum in order to eliminate the remaining traces of solvent or water. The conductivity was measured over the temperature range of -10^0C to 180^0C [26].

S.Panero and B.Scrosati demonstrated that the gel approach can be extended to other ion-conducting membranes in addition to reporting the characteristics of some selected examples of lithium membranes. The electrolyte membranes were prepared by gelling a liquid solution in a polymer matrix. The ionic conductivity of all the membranes was measured by impedance spectroscopy of cells formed by sandwiching the given sample between two blocking stainless-steel electrodes. The electrochemical stability of the lithium-based gel-type membranes was evaluated by measuring their anodic breakdown voltage. The results demonstrate that this, as well as the majority of the lithium membranes have a very high conductivity which ranges from 10^{-3} to 10^{-2} S cm^{-1} at room temperature [27].

Upadhyaya *et. al* prepared a few PMMA based Na^+ ion conducting gel electrolytes by blending the mixture of PMMA+PC and PMMA+(EC+PC) in appropriate ratio with varying $NaClO_4$ concentrations. Good electrical conductivity of nearly 10^{-3} S cm^{-1} was observed at

the temperature of nearly 25^0C [28].

Appetecchi *et. al* prepared polymer gel electrolytes by dispersing selected ceramic powders into a matrix formed by a lithium salt solution contained in a PAN network. The electrochemical characterization demonstrated that these have high ionic conductivity, wide electrochemical stability and high chemical integrity i.e. no liquid leakage even above ambient temperature which makes these suitable as electrolyte separators in lithium ion polymer batteries [29].

Wachtler *et. al* synthesized and characterized several gel membranes of the type PVdF/EC-PC/SiO_2 with and without electrolyte salts by vibrational spectroscopy and by galvanostatic cycling tests. The addition of polymer matrix affects the structure of polymer matrix and not the state of the electrolyte [30].

Gentili *et. al* worked on gel-type lithium conducting polymer electrolytes which resulted that the dispersion of suitable ceramic fillers in PVdF based gel polymer electrolytes gives rise to composite GPEs having some important properties. The fillers did not influence the transport properties but enhanced the mechanical stability as compared to conventional ceramic-free GPEs [31].

Yamamoto *et. al* tested Li-ion polymer batteries (LIPB) with PVdF based gel electrolyte and a liquid electrolyte. It was observed that the PVdF gel electrolyte had high ionic conductivity and completely suppressed oxidation. The PVdF gel electrolytes possess the properties suitable for device applications like high energy density, high permanence and better safety to use [32].

S.S. Sekhon observed that polymer is an important constituent of polymer gel electrolytes along with salt and solvent. The conductivity of lithium ion conducting polymer gel electrolytes decreases with the addition of polymer whereas in the case of proton conducting polymer gel electrolytes an increase in conductivity has been observed with polymer addition. The variation of conductivity of gel electrolytes with temperature shows liquid like behaviour [33].

Iwakura *et. al* investigated the applicability of the polymer gel electrolyte to alkaline secondary batteries such as nickel/metal hydride (Ni/MH) battery prepared from potassium

salt of cross-linked poly (acrylic acid) and KOH aqueous solution. The polymer gel electrolyte was found to have high ionic conductivity and wide potential window almost comparable to the KOH aqueous solution over the wide ranges of KOH concentration and temperature [34].

Kalpana *et. al* fabricated a carbon aero-gel super-capacitor with an alkaline polymer gel electrolyte. The electrolyte acts as a separator which has a conductivity of around 10^{-2} S cm^{-1} at room temperature. The results suggested that an alkaline (KOH)-based gel polymer electrolyte is a prospective improved electrolyte for carbon aero-gel super-capacitors [35].

Flavio S. Freitas *et. al* investigated polymer electrolytes based on mixtures of PEO and an imidazolium-based ionic liquid for dye-sensitized solar cells. The interactions between the copolymer and the ionic liquid were analyzed by infrared spectroscopy and NMR spectroscopy. It was observed that the electrolyte containing 70 wt % of imidazolium has the highest ionic conductivity (2.4 X 10^{-3} S cm^{-1}) [36].

Guangchao Li *et. al* prepared and studied the physical and electrochemical properties of Li-ion conducting poly(vinylidene fluoride-co-hexafluoropropylene) [P(VdF-HFP)]-based gel polymer electrolytes. Phase separation method is used to prepare microporous membranes because of the flexibility of its operation and controllable pore structure [37].

Bookeun Oh *et. al* studied the electrochemical properties of gel polymer electrolytes prepared from poly (vinyl acetate) copolymers. All the gel polymer electrolytes showed elasticity, free standing property and ionic conductivities over 0.5 mS/cm in certain compositions. The gel polymer electrolyte prepared using poly (methyl meth-acrylate-co-vinyl acetate) (PMVC) especially showed stable ionic conductivity over $1x10^{-3}$ S/cm with a reasonable mechanical strength and electrochemical stability above 4.8 V [38].

1.11 OBJECTIVE

In our current project we have tried to prepare a series of polymer gel electrolyte with suitable conductivity by choosing the best composition of blend polymer with a typical salt and solvent. In order to study and understand the behaviour of these materials we studied the formation of the gel electrolytes. Also the structural, micro-structural and electrical properties

are studied using different techniques such as X-ray diffraction, SEM and dielectric spectroscopy.

1.12 ORGANISATION OF THESIS

The thesis consists of four chapters.

Chapter 1 gives an idea about solid state ionics, polymer electrolyte, polymer gel electrolyte along with the past work done on polymer gel electrolyte, literature survey and the main objective of the work is briefly described.

Chapter 2 deals with the different methods of preparation of polymer gel electrolyte and the adopted procedure for preparation i.e. the brief experimental work carried out during the project and the principle of different characterization techniques.

Chapter 3 deals with structural and micro-structural characterization carried out by XRD, SEM. It also gives detailed study of the electrical property of polymer gel electrolyte with the help of impedance spectroscopic analysis at different frequencies. Conductivity is also calculated from the complex impedance plot.

Chapter 4 includes the summary and conclusion of the present work.

Chapter 2

Sample synthesis and characterization techniques

2.1 PREPARATION TECHNIQUES

There are different methods available in literature to prepare different polymer electrolyte. Some of them are explained below.

2.1.1 Solution cast technique:

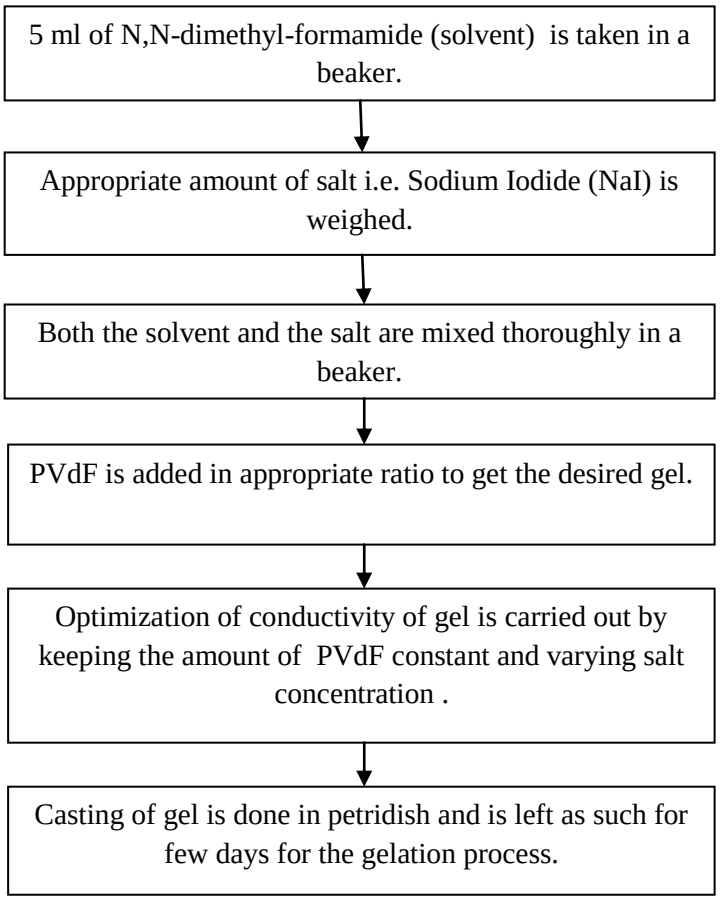
In this method, appropriate amount of polymer and salt are dissolved separately in a polar solvent, and then both of them are poured into a beaker. Using the magnetic stirrer the solutions obtained should be stirred for 10 to 12 hours for complexation of polymer host and salt. The polymer solution is then poured into a petridish and then the free standing polymer electrolyte films will be formed through slow evaporation of the solvent followed by vacuum drying.

2.1.2 Hot press technique:

This technique was proposed by Gray *et. al* [39]. It has many advantages over the solution cast method as it is fast, less expensive and completely dry method for casting polymer electrolyte films. In this technique, dry powders of polymer and complexing salt are mixed in appropriate ratio which is then heated around the melting point temperature of the host polymer for ensuring complete salt complexation. As a result, a soft lump is obtained which is then pressed between two cold metal blocks, resulting a stable polymer gel electrolyte film.

We have prepared the sample by the gelation method which is described by the flowchart given:

2.1.3 Flowchart showing the preparation of gel electrolyte by the gelation method



Materials under investigation:

1. **Solvent (DMF):** We have chosen N,N-dimethyl-formamide as the solvent i.e. $(CH_3)_2NC(O)H$. It has –O group which participates in the formation of the coordinate bond. It has a higher dielectric constant that helps in the dissolution of salt.

2. **Polymer (PVdF):** The polymer that we have taken is poly (vinylidene-fluoride) i.e ---$-(C_2H_2F_2)_n-$. It has low cohesive energy which exhibits high flexibility. It has high molecular weight and provides high mechanical stability, thermal stability and chemical stability.

3. **Salt (NaI):** The anionic part of the salt that we have chosen is bulky as compared to the cationic part. So the cationic part i.e. Na^+ comes out easily and thus provides ions for conduction. The salt possesses low lattice energy too.

For making different compositions of polymer gel electrolyte of different compositions the following formula is used.

$$\frac{O}{Na} = \left(\frac{mass\,of\ solvent}{mass\,of\ salt}\right) \times \left(\frac{mol.wt.of\ salt}{mol.wt.of\ solvent}\right) \times n$$

where, n= number of active oxygen.

2.2 CHARACTERISATION TECHNIQUES:

The polymer gel electrolyte was characterized using a variety of analytical techniques. The confirmation of salt complexation was carried out using XRD analysis. XRD studies also give the information on the structural aspect like crystallinity, amorphosity, chain length etc. Scanning electron microscopy (SEM) provides surface morphological information of the films. The electrical conductivity measurements are usually carried out by impedance spectroscopic technique to understand the electrical properties of the materials.

2.2.1 X-Ray Diffraction(XRD) study:

X-ray diffraction method is a rapid analytical technique primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions. The interaction of the incident rays with the sample produces constructive interference when conditions satisfy Bragg's law i.e. $n\lambda = 2d \sin\theta$.

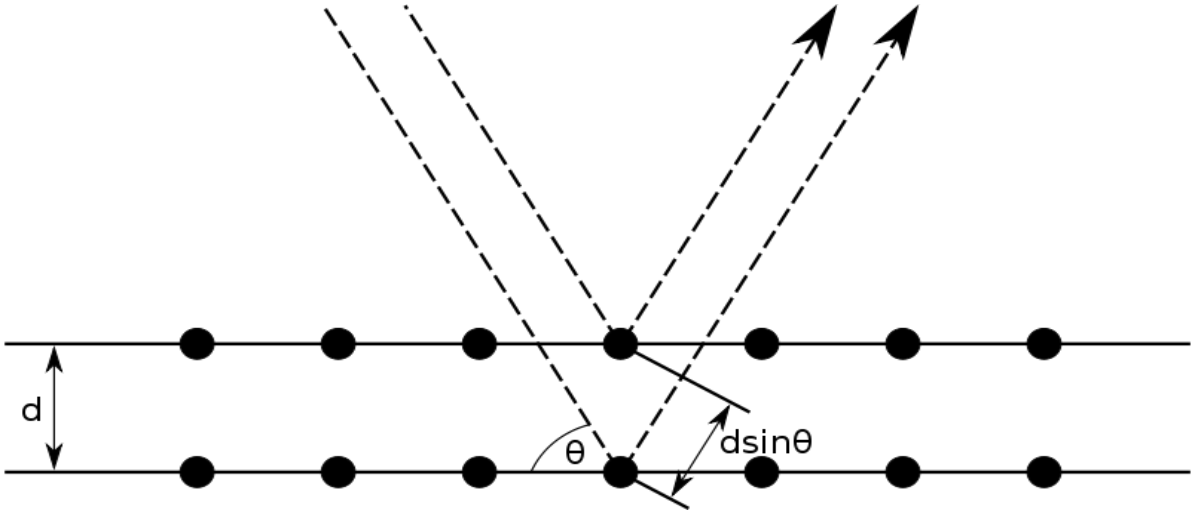


Fig.2.1. Schematic diagram showing Bragg's law

This law relates the wavelength of electromagnetic radiation to the diffraction angle and the

lattice spacing in a crystalline sample. These diffracted X-rays are then detected, processed and counted. By scanning the sample through a range of 2θ angles, all the possible diffraction directions of the lattice should be attained due to random orientation of the powdered material.

From the XRD data we can (i) measure the average spacing between the layers or rows of atoms, (ii) determine the orientation of a single crystal or grain, (iii) find the crystal structure of an unknown material and (iv) measure the size, shape and internal stress of small crystalline regions and also it gives information about crystallinity, amorphosity and chain length of amorphous polymeric materials. We have also calculated the inter-planar spacing, d using the Bragg's law as explained above and also the inter-chain separation of the polymer.

2.2.2 Scanning electron microscopy (SEM):

Scanning electron microscope uses a focused beam of high energy electrons to generate signals at the surface of the specimen. The signals obtained from electron-sample interactions give information about the sample including external morphology, chemical composition and crystalline structure and orientation of materials. These signals coming due to electron-sample interactions from the sample surface include secondary electrons, backscattered electrons, the characteristic X-rays. Secondary electrons and backscattered electrons are commonly used for imaging samples; most valuable for showing morphology and topography on samples and backscattered electrons are most valuable for rapid phase discrimination. SEM analysis is considered to be non-destructive; it is possible to analyze the same material repeatedly.

2.2.3 Dielectric spectroscopy:

Dielectric spectroscopy is the measurement of relaxation phenomena that are related to the presence of dipoles in samples i.e. it measures the dielectric properties of a medium as a function of frequency [40-42]. This technique also measures the impedance parameters of a system over a wide range of frequency. The dielectric study explains the electrical properties of the sample and also it gives the a.c. conductivity variation with the frequency. From the complex impedance plot we can find the bulk resistance and further the d.c. conductivity of the sample. This can be used for the measurement of structural and interfacial properties of gels.

Chapter 3

Results and discussion

3.1 X-Ray Diffraction (XRD) Analysis

The X-ray diffraction studies were carried out in order to confirm the formation of the material and its phase identification using a Philips X'Pert 1 X-Ray Diffractometer. The x-ray diffractogram of the sample was recorded at room temperature using Cu-K_α radiation (λ=1.5418 A^0) at a scan speed of 3^0 min^{-1} in the range of Bragg angles 2θ ($10^0 \leq 2\theta \leq 40^0$).

XRD pattern of polymer gel electrolyte for different compositions:

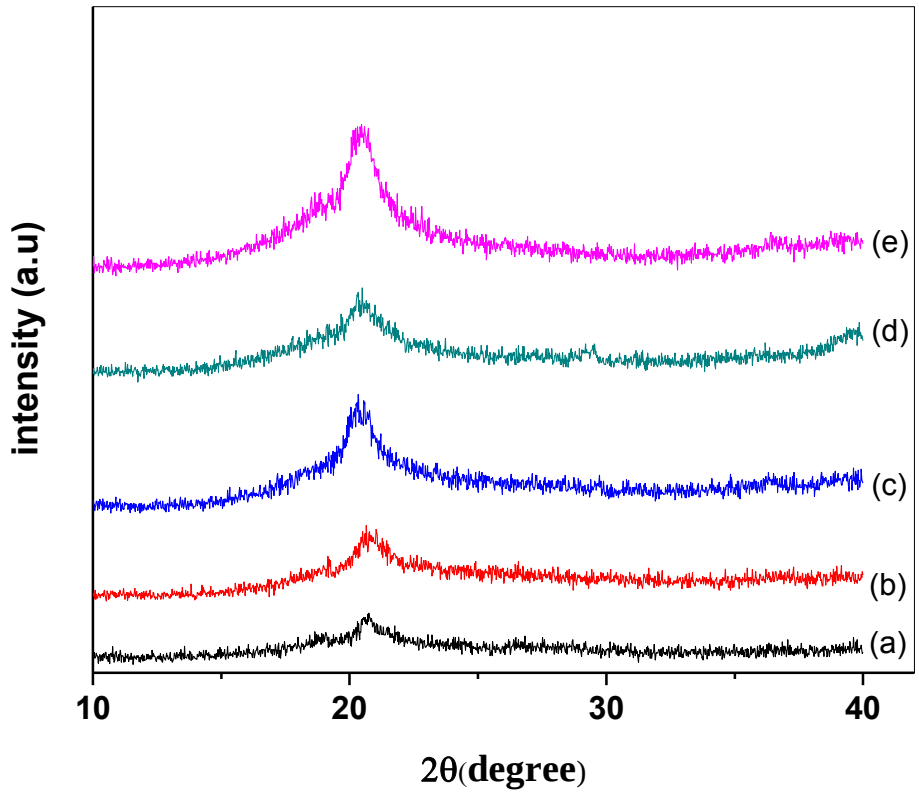


Fig.3.1 (a) O /Na=20, (b) O/Na=40, (c) O/Na=60, (d) O/Na=80, (e) O/Na=100

In the present study, XRD analysis has been carried out to get information about the crystallinity, inter-planar spacing and the inter-chain separation of the polymer gel electrolyte. The figure shows the XRD pattern of polymer gel electrolyte for various compositions of O/Na. The typical XRD patterns of all the polymer gel electrolytes are nearly

same except the intensity of the crystalline peak. The crystalline peak for O/Na=100 is the sharpest as compared to others denoting most crystalline among all the studied gel electrolyte. The appearance of peak over the broad humps indicates the semi-crystalline nature of the samples. The inter-planar spacing, d is calculated by Bragg's law, $n\lambda=2d\sin\theta$, where n=order of diffraction, λ=wavelength of x-ray (1.5418 A^0) and θ=angle of diffraction.

In case of polymer sample the strong innermost peak is considered to arise from the inter-atomic vectors between adjacent chains. On the basis of assumption the inter-chain separation can be calculated from the position of the first diffraction maximum using the following equation:

$$R = \frac{5}{4} \times \frac{\lambda}{2} \frac{1}{Sin\theta} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

$$R = \frac{7}{2\pi} \times \frac{\lambda}{2Sin\theta} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

The inter-chain separation calculated from (1) is suitable for short chain polymers whereas (2) is suitable for highly oriented amorphous linear polymer [43].

Table 3.1 To calculate the inter-chain separation and inter-planar spacing:

O/Na	2Θ (degrees)	Inter-chain separation R=(7/2∏)*(λ/2Sinθ) (A^0)	Inter-planar spacing, d=λ/(2Sinθ) (A^0)
20	**20.63**	**4.7989**	**4.3053**
40	**20.79**	**4.7623**	**4.2725**
60	**20.39**	**4.8547**	**4.3554**
80	**20.44**	**4.8429**	**4.3449**
100	**20.40**	**4.8524**	**4.3533**

3.2 Scanning Electron Microscopy (SEM):

The surface properties of the materials have been studied using JEOL JSM-6480LV SEM. The sample was platinum coated prior to being scanned under high-resolution field emission gun scanning electron microscope.

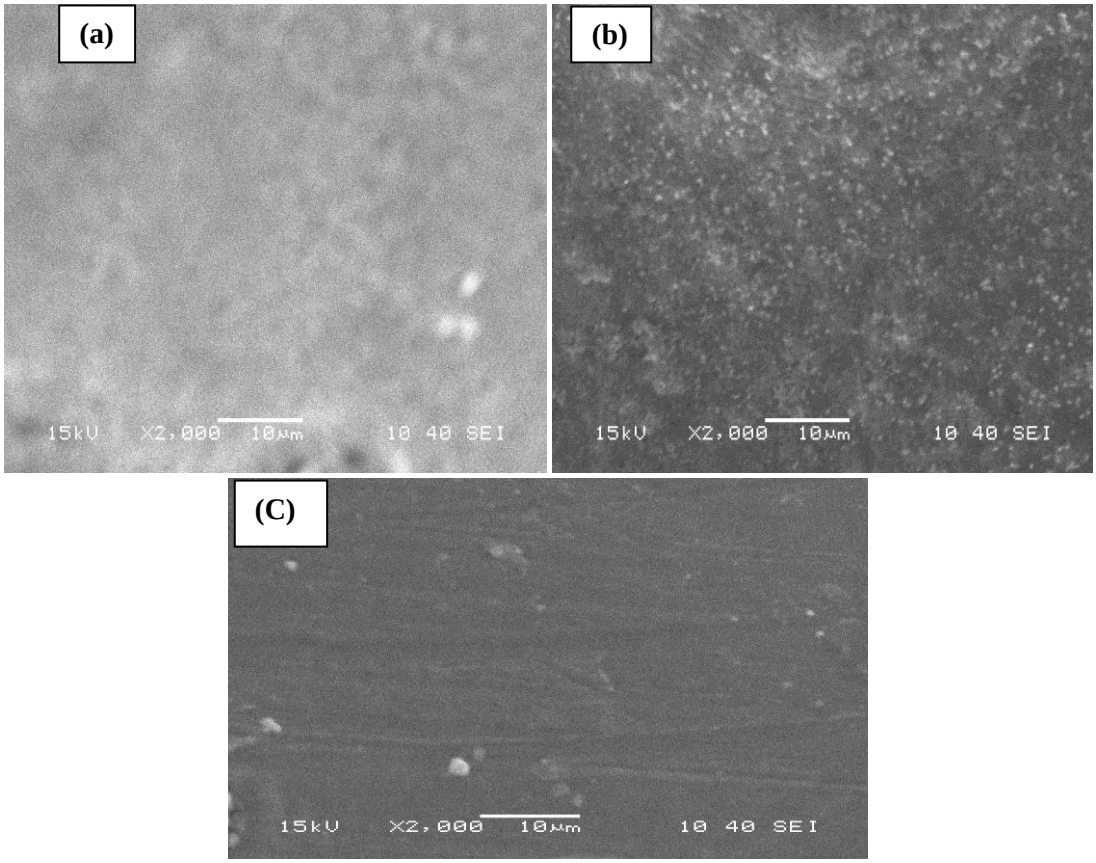


Fig.3.2 (a) O/Na=40 at 2000X (b) O/Na=60 at 2000X (c) O/Na=100 at 2000X

The figure shows the scanning electron micrographs of PVdF based polymer gel electrolyte samples for different compositions. It is observed that as we go on increasing the composition, the surface roughness is increasing which is closely linked with crystallinity. Decrease in the concentration of salt i.e. by increasing the O/Na ratio results in appearance of more surface roughness. Increase in surface roughness indicates the increase in crystalline nature of the sample. So, for higher compositions the sample is becoming more crystalline which is in accordance with the results of XRD analysis.

3.3 Dielectric study:

The impedance measurements were carried out using PSM 1735 Impedance analysis Package Newton 4th Limited in the frequency range of 100 mHz to 1 MHz. The impedance spectra of the sample (SS| PGE| SS) were recorded with an input signal of amplitude 100 mV at room temperature. The impedance data so obtained was analyzed using different formalism and thus the conductivity of the sample was calculated.

3.3.1 Dielectric constant versus frequency graph:

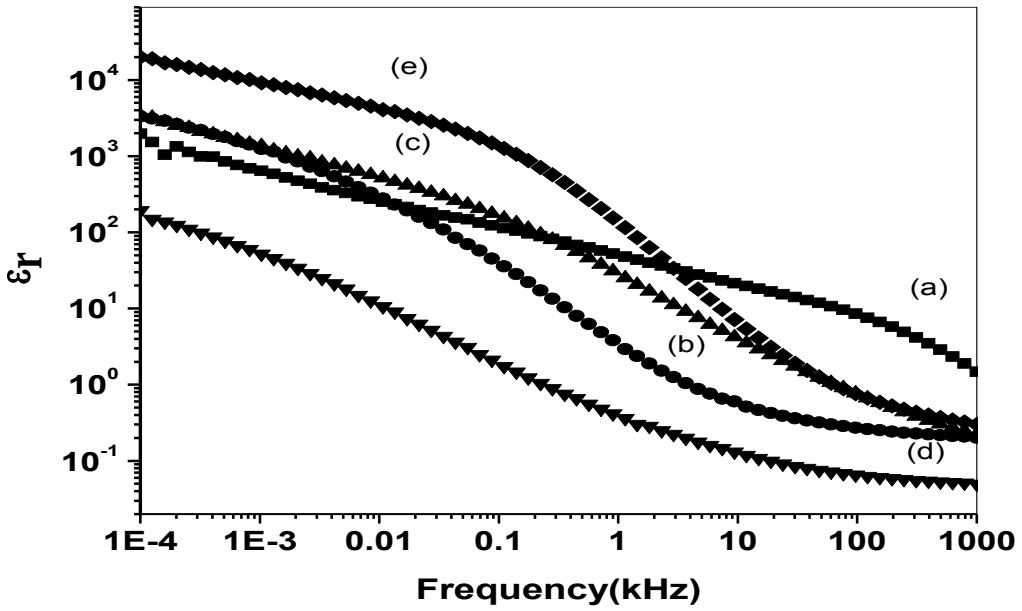


Fig.3.3 (a) O/Na=20, (b) O/Na=40, (c) O/Na=60, (d) O/Na=80, (e) O/Na=100

This graph shows the variation of relative dielectric permittivity (ε_r) with frequency for different compositions. At lower frequency, ε_r has higher values which decreases sharply with increase in frequency. For all samples, ε_r decreases on increasing frequency which may be attributed to the electrical relaxation processes. At low frequency region, ε_r decreases due to electrode polarization. At high frequency region, we observe a plateau for all polymer gel electrolytes except O/Na=20.

3.3.2 Tangent loss versus frequency graph:

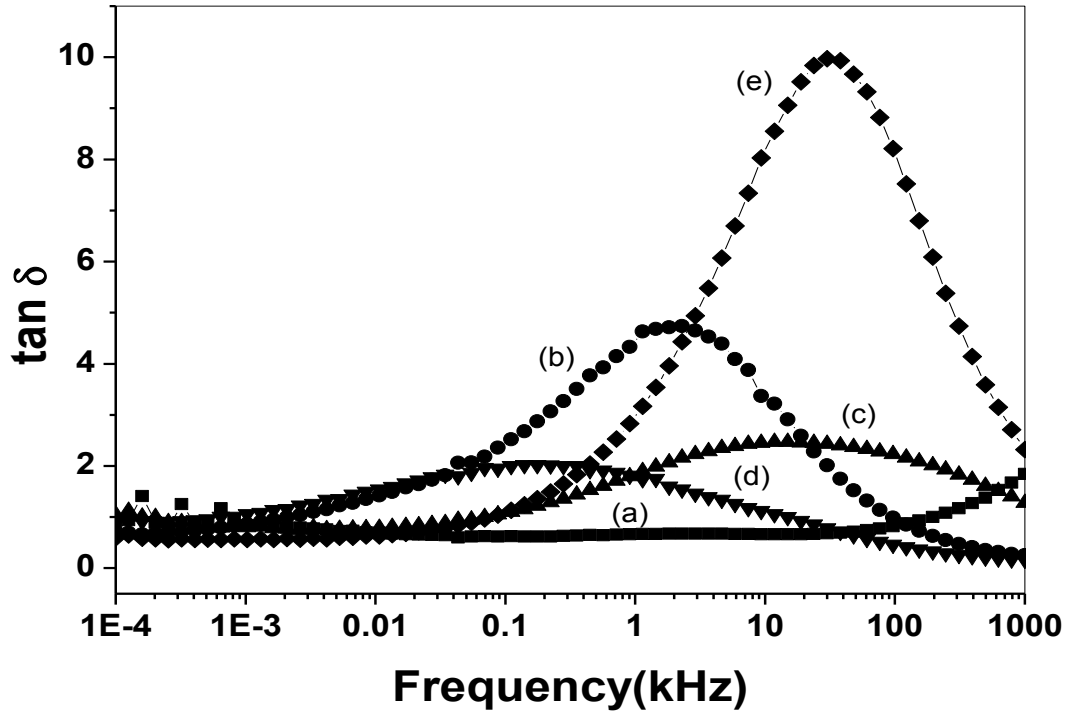


Fig. 3.4 (a) O/Na=20, (b) O/Na=40, (c) O/Na=60, (d) O/Na=80, (e) O/Na=100

Fig.3.4 shows the variation of tangent loss with frequency for different compositions of the prepared polymer gel electrolyte samples. For each composition except O/Na=20, a peak is observed at a certain frequency. The peak position is different for different compositions. The appearance of peaks suggest the presence of relaxing dipoles in the samples.

3.3.3 a.c. conductivity versus frequency graph:

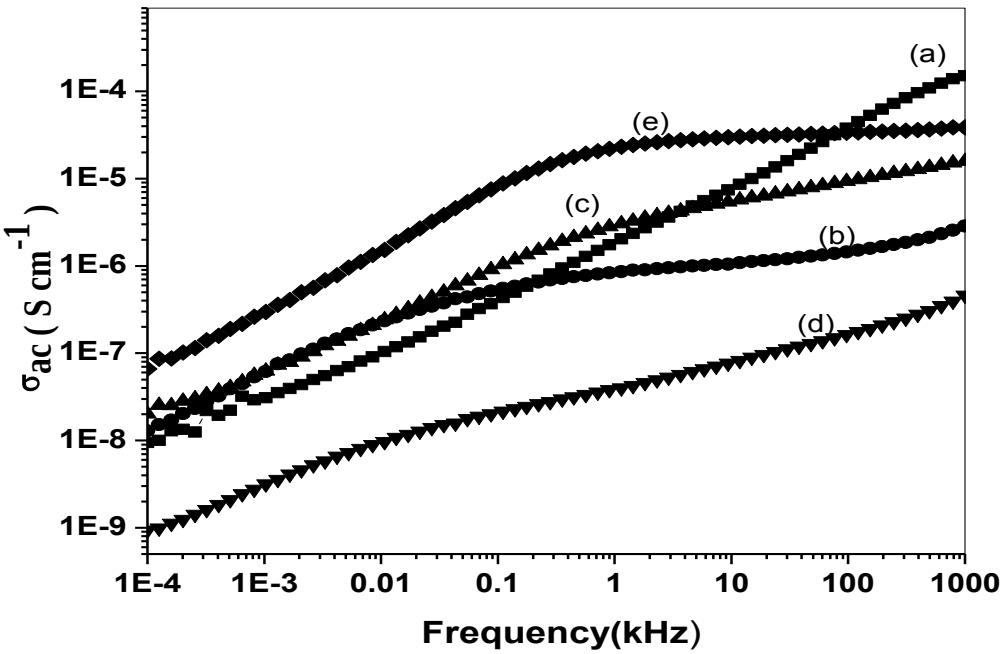


Fig.3.5 (a) O/Na=20, (b) O/Na=40, (c) O/Na=60, (d) O/Na=80, (e) O/Na=100

This graph shows the variation of σ_{ac} with frequency for the different concentrations. The a.c. conductivity was calculated using the relation, $\sigma_{ac}=2\prod f\ \varepsilon_r\varepsilon_0 \tan\delta$, where $2\prod f = \omega$=angular frequency. The a.c. conductivity patterns show a frequency independent plateau in the high frequency region and exhibits dispersion in the lower frequency region. Low frequency region is due to the electronic polarization which is due to the free ions. The high frequency plateau indicates the d.c. conductivity of the electrolyte.

3.3.4 Z' versus Z" graph:

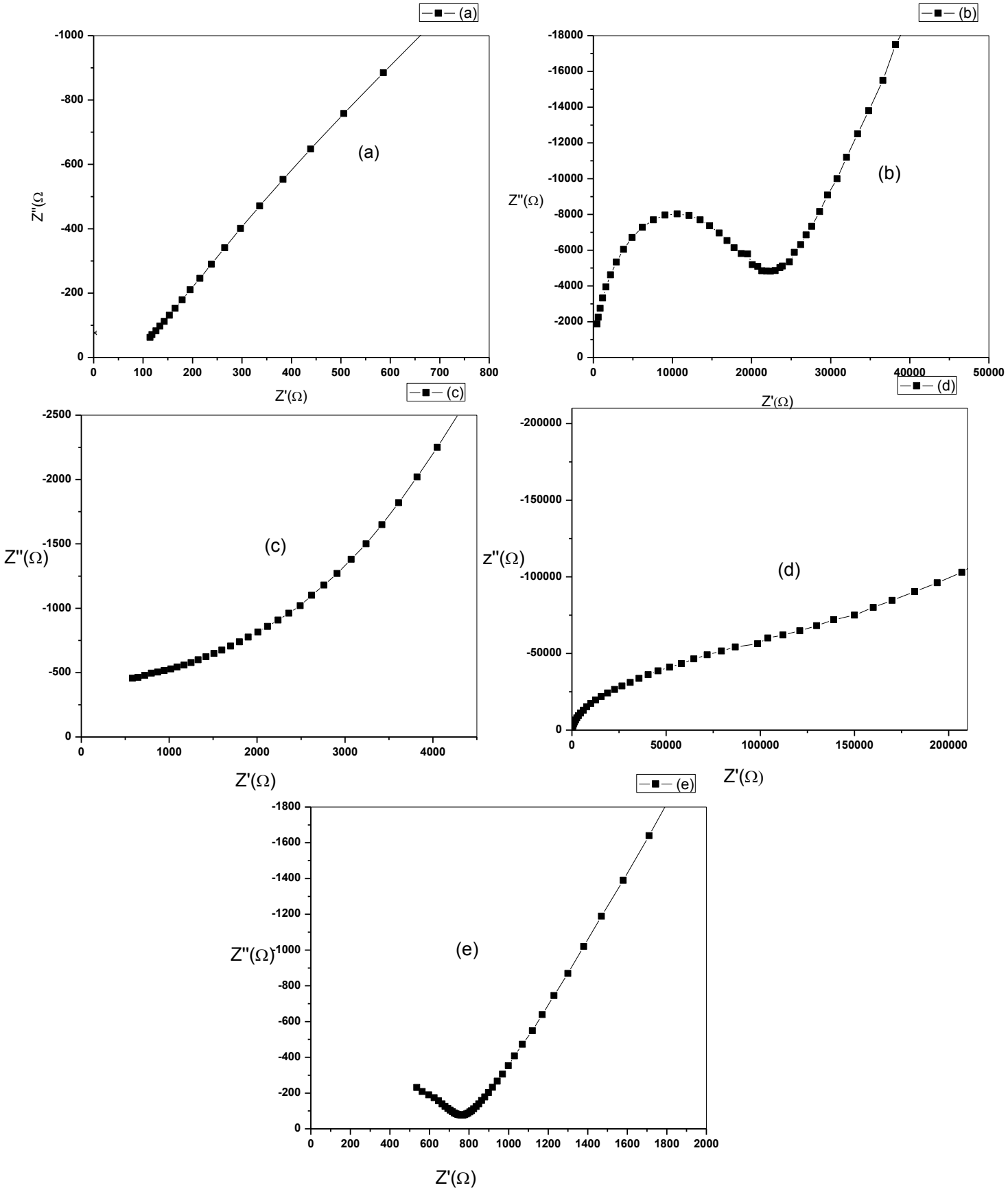


Fig.3.6 (a) O/Na=20, (b) O/Na=40, (c) O/Na=60, (d) O/Na=80, (e) O/Na=100

The above figures represent the complex impedance spectra/Nyquist plot of gel films for various concentrations. The typical Nyquist plot of the samples for few compositions comprises of a broadened semicircle in the higher frequency region followed by a tail or spike in the lower frequency region. The higher frequency semicircle can be ascribed mainly to the bulk property of the material whereas the low frequency spike indicates the presence of double layered capacitance at the metal-electrode interface [44]. The intercept of the semi-circle with the real axis (Z') gives rise to the bulk (ionic) resistance R_b of the materials.

We have calculated the d. c. conductivity using the relation:

$$\sigma_{dc} = \frac{1}{R_b} \times \frac{l}{A}$$

where, σ_{dc} is the d.c. conductivity, R_b is the bulk resistance in ohm, l is the thickness of the polymer gel electrolyte and A is the area of the electrode.

Table 3.2 <u>d.c. conductivity for different compositions:</u>

O/Na	σ_{dc} (S cm^{-1})
20	$5.6X10^{-4}$
40	$2.2X10^{-6}$
60	$3.5X10^{-5}$
80	$6.1\ X10^{-7}$
100	$8.2\ X10^{-5}$

From the table it is observed that, the maximum d. c. conductivity was found to be **$5.6X10^{-4}$** S/cm for O/Na=20.

Chapter-4

Conclusion and Summary

A series of polymer gel electrolyte were prepared by gelation method by taking different compositions of the salt with respect to solvent and polymer. The XRD studies indicated the presence of both the crystalline and amorphous phase thereby concluding the sample to be semi-crystalline in nature. The scanning electron micrographs confirmed the results obtained from the XRD analysis. The complex impedance study of the sample indicated the bulk property of the material in the high frequency region and from bulk resistance d.c. conductivity was calculated. The d.c. conductivity of the material is found to be highest for O/Na=20. The a.c. conductivity of the material shows both low frequency dispersion and high frequency plateau region. The low frequency region attributes to the electrode polarization and the high frequency region is due to the d. c. conductivity. The appearance of dielectric loss peak in dielectric loss versus frequency plot indicates that the relaxation is dipolar in nature. Thus, we can conclude that the polymer gel electrolyte needs further research to get an enhanced conductivity as compared to the liquid electrolyte.

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